

# Transmission Through Carbon Nanotubes With Polyhedral Caps

M. P. Anantram and T. R. Govindan

*NASA Ames Research Center, Mail Stop T27A-1, Moffett Field, CA, USA 94035-1000*

## Abstract

We study electron transport between capped carbon nanotubes and a substrate, and relate this transport to the local density of states in the cap. Our results show that the transmission probability mimics the behaviour of the density of states at all energies except those that correspond to localized states. For a capped carbon nanotube that is not connected to a substrate, the localized states do not couple to the coexisting continuum states. However, close proximity of a substrate causes hybridization between these states. As a result, new transmission paths open from substrate states to nanotube continuum states via the localized states in the cap. We show that the interference between various paths gives rise to transmission *antiresonances* with the minimum equal to zero at the energy of the localized state. The presence of defects in the tube placed close to the cap transforms antiresonances into resonances. Depending on the spatial position of defects, these resonant states are capable of carrying a large current. The results of this paper are of relevance to carbon nanotube based studies on molecular electronics and probe tip applications.

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## I. INTRODUCTION

The tip of a carbon nanotube (CNT) can either be open or capped. Methods of constructing polyhedral caps have been suggested<sup>1</sup> and there has been recent evidence for the existence of caps in fabricated nanotubes.<sup>2-4</sup> Characteristic features of electron flow through CNT is of relevance to both molecular electronics and experiments using CNT tips as a probe.<sup>6-8</sup> To the best of our knowledge, there have been no studies of electron transmission through a CNT cap, although there have been studies of the local density of states (LDOS) in a CNT with caps.<sup>2,3</sup> Our study clarifies the relationship between the LDOS and electron transmission in CNT with polyhedral caps. In this paper, we study the physics of transport through capped CNT and address the following issues: (i) the relationship between LDOS and transmission probability through cap atoms, (ii) the effect of the localized discrete energy levels in the cap, and (iii) the effect of defects on tunnel current/transmission.

Incident electron waves from the CNT tunnel via the cap to the substrate. The wave functions of the cap and substrate overlap due to their physical proximity.<sup>9</sup> This overlap provides a physical mechanism for hybridization of localized and continuum states, which transform these initially localized states (discrete energy levels) to quasi-localized states. As a result of this hybridization, new channels involving the quasi-localized states open up for electron transmission from substrate to CNT. In this study, we focus on the truly metallic armchair tubes, which show promise as quantum wires and for CNT based probes involving a tunnel current. The 5-fold symmetric polyhedral cap with one pentagon at the cap center and five pentagons placed symmetrically along the edge of a (10,10) nanotube is considered in this study [Fig. 1].

## II. THEORY

In this section we outline the formalism used and also discuss the assumptions made in our study. The combination of CNT and substrate can be conceptually divided into three

parts: substrate (**S**), section of CNT including the cap (**D**) and a semi-infinite CNT region (**L**) [Fig. 2(a)]. The location of the interface between **D** and **L** is arbitrary. The transmission and LDOS are calculated using the Green's function formalism.<sup>10,11</sup> The Green's function  $G^r$  is obtained by solving:

$$[E - H - \Sigma_L^r - \Sigma_S^r] G^r(E) = I, \quad (1)$$

where  $H$  is the Hamiltonian of **D**.  $\Sigma_L^r$  and  $\Sigma_S^r$  are the self-energies due to the semi-infinite CNT and substrate respectively. The single particle LDOS at site  $i$  [ $N_i(E)$ ] and transmission probability [ $T(E)$ ] at energy  $E$  are obtained by solving Eq. (1) for the diagonal element  $G_{ii}^r$  and the off-diagonal sub-matrix of  $G^r$  corresponding to atoms in **D** that couple to **L** and **S**:

$$N_i(E) = -\frac{1}{\pi} \text{Im}[G_{ii}^r(E)] \quad (2)$$

$$T(E) = \text{Trace}[\Gamma_L G^r \Gamma_S G^a] . \quad (3)$$

$\Gamma_L$  and  $\Gamma_S$  are coupling rates to the semi-infinite CNT<sup>11</sup> and substrate respectively.  $\Gamma_S$  depends on the overlap matrix elements between sites in the tip and substrate.  $\Sigma_S^r$  is a complex number and its imaginary part  $\Gamma_S$  represents injection of electrons from **S** to **D**. The real part of  $\Sigma_S^r$  causes a change in onsite potential and thus is neglected in our study. For simplicity, we take  $\Gamma_S$  to be an energy independent parameter. This is often the case over small ranges of energy. Also, this assumption allows us to focus on studying the physics of the cap, rather than a convolution of the density of states of the tip and substrate.

For tubes with defects, we consider the bond rotation defect which creates two pentagon-heptagon pairs (see box in Fig. 1).<sup>12</sup> Finally, the numerical calculations use the single orbital real space tight binding representation of the CNT Hamiltonian,<sup>13</sup>

$$H = -b \sum_{i \neq j} c_i^\dagger c_j + c.c. , \quad (4)$$

where each carbon atom has a non zero hopping parameter  $b$  with its three near neighbors, and  $c_i$  ( $c_i^\dagger$ ) is the annihilation (creation) operator at atomic site  $i$ .

### III. RESULTS AND DISCUSSION

The main issues addressed in this section are: (i) relationship between the LDOS and the transmission probability through cap atoms in a defect free CNT, (ii) the effect of the localized discrete energy levels in the cap, and (iii) the effect of defects on tunnel current/transmission.

We first address issues (i) and (ii) involving defect free caps by studying the relationship between the LDOS at atom  $i$  in the cap and the transmission probability from the substrate to the semi-infinite CNT via atom  $i$ . The LDOS at various atomic locations in the cap are plotted in Fig. 3 for the case when a cap atom does (dashed) / does not (solid) make contact with the substrate. When the cap does not make contact with the substrate, the resonant peaks in the LDOS are absent because the localized states have an infinite lifetime.<sup>5</sup> Coupling of the cap to the substrate causes hybridization of the localized and continuum states. As a result, the localized states become quasi-localized with a finite lifetime. This is represented by the broadened resonances in Fig. 3. In the energy range considered, there are two localized states, one around 0.25 eV and the other around -1.5 eV.

We find that the LDOS varies significantly with atomic location, with the LDOS at the apex atom 1 being almost an order of magnitude smaller than the LDOS of atom 4 which is at the cap edge. The LDOS of atoms 2 and 3 which lie inbetween, and the DOS averaged over all cap atoms are also shown in Fig. 3 for comparison. When coupling to the substrate is weak, the transmission probability is correspondingly much larger when atom 4 makes contact to the substrate (Fig. 4). We also find that the transmission probability mimics the LDOS at most energies, as is seen for the four cap atoms considered [Fig. 4]. The major difference is at the resonant energy, where *the LDOS peaks corresponds to transmission zeroes*. The transmission dip arises from hybridization of localized and continuum states via coupling to the substrate as represented pictorially in Fig. 2(b). States in the CNT cap comprise of localized ( $\phi_L$ ) and continuum ( $\phi_C$ ) states that are uncoupled from each other. Bringing the substrate in close proximity to the cap couples  $\phi_L$  and  $\phi_C$  to the substrate

states ( $\phi_S$ ). As a result, electrons have many paths to be transmitted from  $\phi_S$  to  $\phi_C$ : (i) directly from  $\phi_S \rightarrow \phi_C$ , (ii)  $\phi_S \rightarrow \phi_L \rightarrow \phi_S \rightarrow \phi_C$  and (iii) higher order representations of (ii). The interference between these paths gives rise to the transmission zeroes at the resonant energies (inset of Fig. 4). A similar effect has been studied before in the context of scattering of light from molecules<sup>14</sup> and electron transport in stubbed semiconductor wires.<sup>15</sup> When the strength of coupling between the cap and substrate increases, the antiresonances become stronger. That is, the minimum is still zero but the width scales with coupling strength  $\Gamma_s$  as shown in Fig. 5.

We now consider changes to the antiresonance picture due to defects in a tube [issue (iii)]. A defect locally mediates mixing/hybridization of localized and continuum states. Quasi-localized states ( $\phi_L$ ) are now coupled to continuum ( $\phi_C$ ) and substrate states ( $\phi_S$ ). This leads to transmission paths similar to a double barrier resonant tunneling structure [Fig. 2(c)]. In addition, the paths leading to the transmission antiresonance discussed previously also exist, and are accounted for in the calculations.

We consider a topological bond rotation defect (box in Fig. 1).<sup>12</sup> The LDOS remains similar to Fig. 3 but in comparison to Fig. 4, the transmission probability has changed significantly around the localized energy levels as shown in Fig. 6. Resonant peaks appear in the transmission probability for the same reasons discussed in the previous paragraph. In the presence of a defect, the resonance width is determined by two contributions. The first contribution is the hybridization due to the substrate and the second contribution is the hybridization due to the defect. The second contribution depends on  $|\langle \phi_C | H_{defect} | \phi_L \rangle|$ , where  $H_{defect}$  is Hamiltonian of the defect.  $|\phi_L|^2$  (or the density of states of the localized state) decays with distance away from the cap. As a result, the width of the transmission resonance depends on location of the defect. Fig. 6 shows the transmission for different distances of the defect from the cap ( $L_D$ ).  $L_D$  equal to 7, 15 and 35 in units of the one dimensional unit cell length of armchair tubes. The main feature is that the *width becomes smaller as distance of the defect from the cap increases*. This can be understood from the fact that the strength of hybridization between continuum and localized states in the

cap arising due to the defect ( $|\langle \phi_C | H_{\text{defect}} | \phi_L \rangle|$ ) decreases as distance of the defect increases from the cap apex. In terms of the current carrying capacity, clearly from Fig. 6, the resonant state is capable of carrying a large current per unit energy compared to the background energies. Thus, engineering spatial defects can enhance the current injected into a nanotube.

In addition to the transmission resonance around  $0.25\text{eV}$ , there is a new narrow resonance around  $0.5\text{eV}$  in Fig. 6. This new resonance is due to quasi-localized states associated with the bond rotation defect.<sup>16</sup> To demonstrate this, the DOS averaged over an annular ring at the location of the defect ( $L_D = 7$ ) and the DOS averaged over a cap without defects (as in Fig. 4) are plotted in Fig. 7. Clearly, the resonance around  $0.25\text{ eV}$  is due to the quasi-localized state in the cap. The narrow transmission resonances around  $0.5\text{ eV}$  in Fig. 6 correspond to the large DOS resonance in the same energy range (Fig. 7) when there is a bond rotation defect.

#### IV. CONCLUSIONS

We studied phase coherent transport through carbon nanotube tips making contact to a substrate. The transmission probability mimics the LDOS for energies away from that of the localized states in the CNT cap. The LDOS at, and transmission from an atom at the cap apex are almost an order of magnitude smaller than those for an atom at the cap edge. At energies of the localized cap states, the transmission probability exhibits a strong antiresonance. Defects in the tube alter this antiresonance by providing additional defect-assisted channels for transport into the continuum states of the CNT. As a result, the transmission probability shows a resonance. Our calculations show that the resonant levels are capable of carrying large amounts of current compared to other energies and so are relevant to experiments that measure the tunnel current via carbon nanotube based tips. The current carrying capacity of these resonances depend on the position of the defect with a defect closer to the cap producing a larger current.

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- <sup>16</sup> We have calculated LDOS and transmission in an isolated arm chair tube with a bond rotation defect. Quasi-localized states at the defect exist around 0.5eV.



### Figure Captions:

**Fig. 1:** (10,10) carbon nanotube with a polyhedral cap. The dashed lines connect equivalent sites of the cap and nanotube in this two dimensional representation. The dashed box shows a bond rotation defect.

**Fig. 2:** (a) The CNT-substrate system is divided into three regions **S**, **D** and **L**. (b) In the absence of defects, the localized and continuum states in the nanotube are decoupled. Coupling between the substrate and cap causes opening of transport paths where an electron incident in the substrate tunnels into and out of the localized state before being scattered into the continuum. This results in an antiresonance. (c) The presence of defects in the tube opens additional transport paths similar to those in double barrier resonant tunneling structures, with coupling to substrate and scattering by the defect acting as the two scattering centers. This transforms the transmission antiresonance in (b) to a resonance.

**Fig. 3:** LDOS of atoms at the apex of the cap (atom 1), edge of the cap (atom 4), and at locations inbetween (atom 2 and 3). The solid and dashed lines represent the LDOS with and without coupling to the substrate. The resonant peaks (dashed line) correspond to localized states in the cap atoms that have become quasi-localized due to coupling with the substrate. The solid lines do not show this peak because these states are truly localized when there is no coupling to the substrate.

**Fig. 4:** Transmission probability versus energy for a CNT without defects in contact with a substrate [Fig. 2(b)]. The antiresonances occur at the same energy as the LDOS resonances in Fig. 3. The inset shows an expanded view of the antiresonance, which was computed for a coupling strength of  $\Gamma_S = 2.5\text{meV}$ .

**Fig. 5:** The width of the antiresonance increases with strength of coupling  $\Gamma_S$  but the minimum is always zero. The value of  $\Gamma_S$  is given in the legend. The dotted and dashed curves are scaled by 25 and 5 times the computed transmission probability respectively.

**Fig. 6:** Transmission probability versus energy in presence of a bond rotation defect. Note that the very strong resonance caused by an appropriately placed defect is capable of carrying large current. For this calculation, the defect coupling strength was  $\Gamma_S = 1.0\text{meV}$ .

**Fig. 7:** Average DOS of an annular ring containing the defect. The resonance around 0.5eV corresponds to a quasi-localized state of the defect. The resonance around 0.25eV corresponds to the quasi-localized cap states.

# FIGURES

Fig. 1/ Anantram

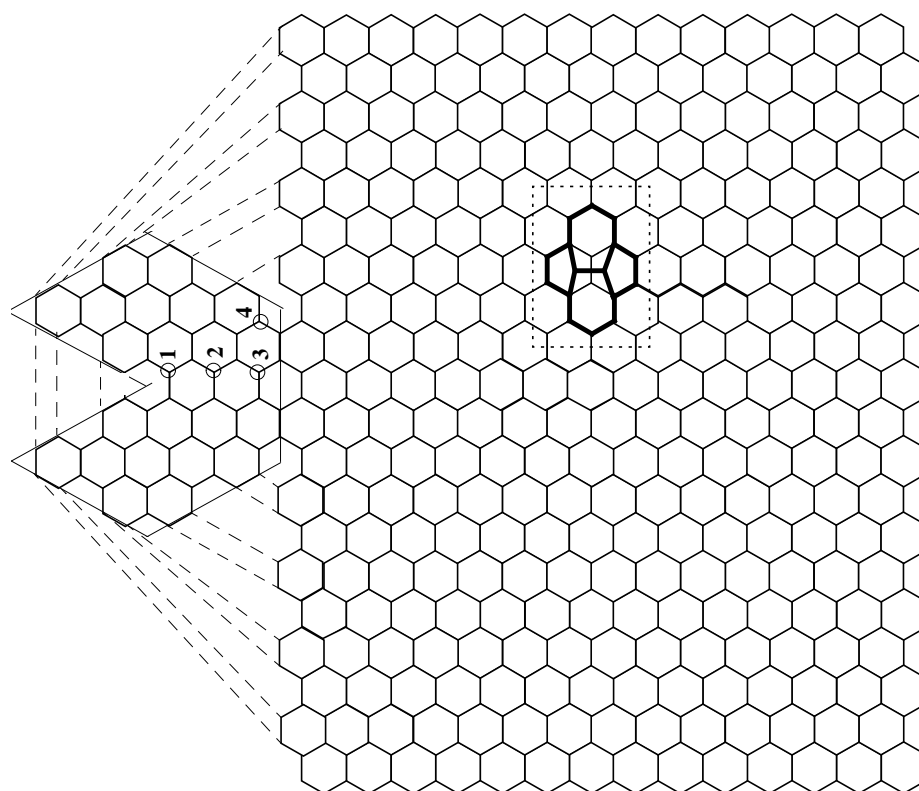


Fig. 2 / Anantram

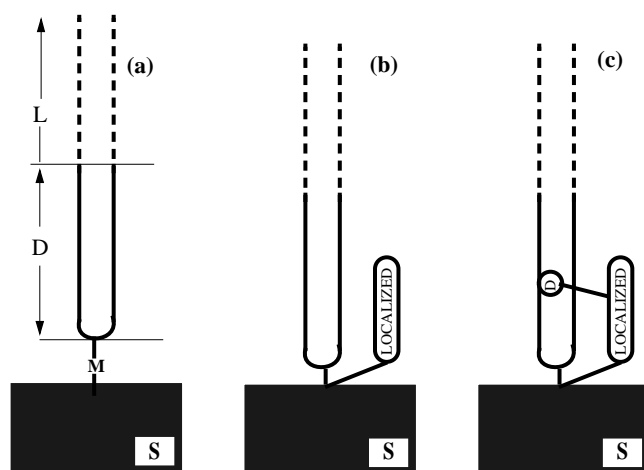


Fig. 3 / Anantram

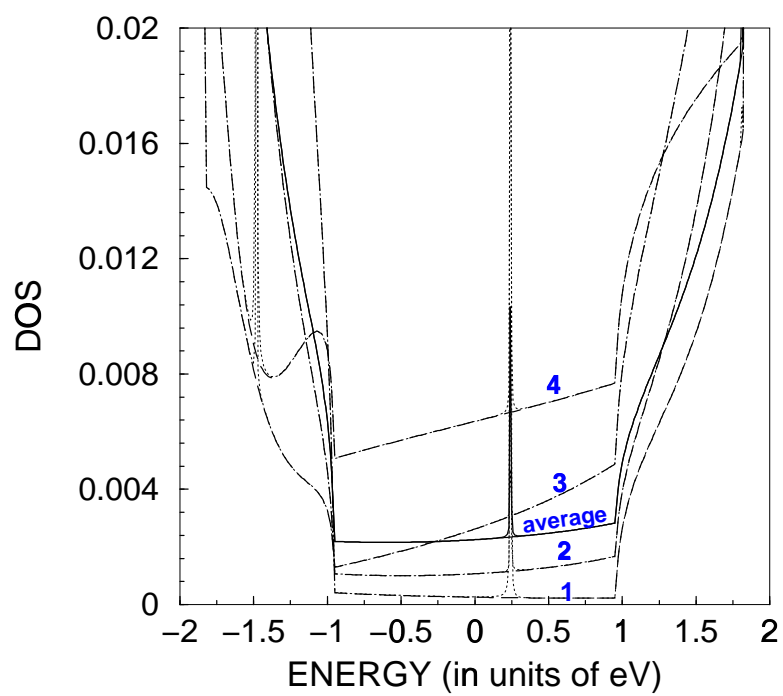
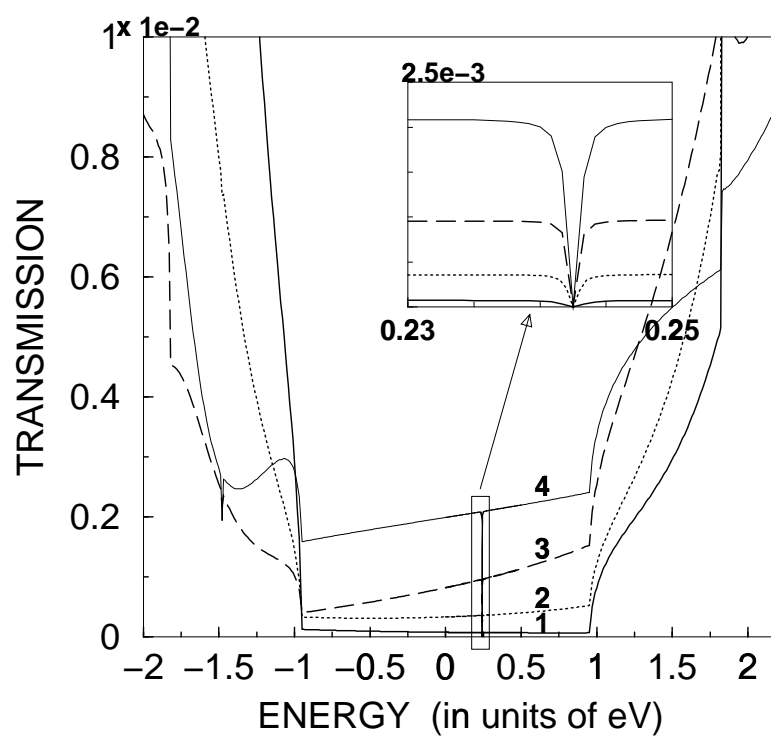


Fig. 4 / Anantram



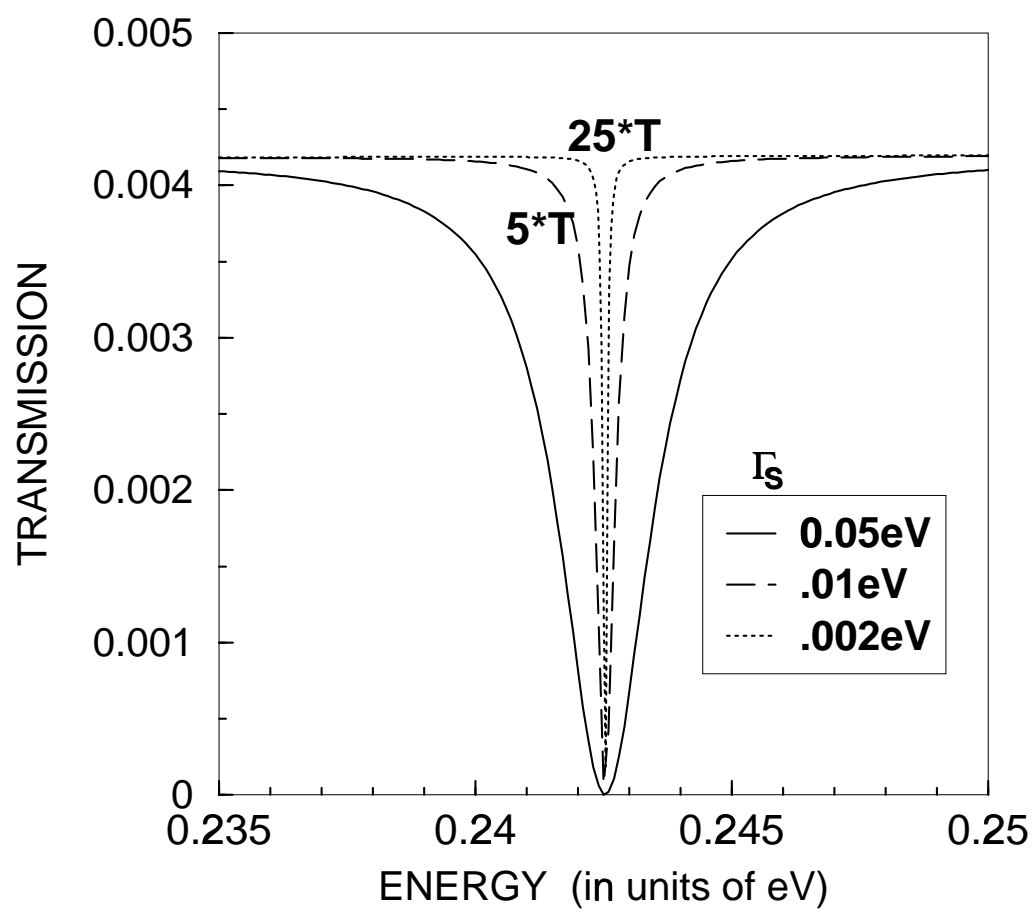


Fig. 6 / Anantram

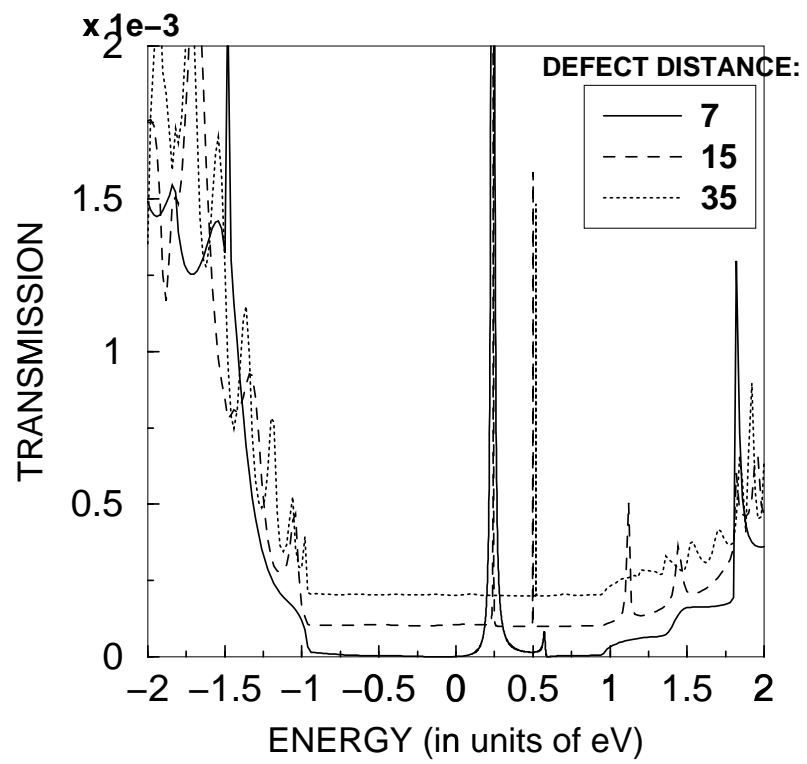




Fig. 7 / Anantram

